COMMENT

Reduction of Wavenumbers of Pure Rotational and Vibration–Rotational Transitions of LiH in the Electronic State $X^{1}\Sigma^{+}$

In a previous paper (1) we illustrated a discussion of adiabatic and nonadiabatic effects in vibrational-rotational spectra of diatomic molecules with an analysis of spectral data of LiH in the electronic ground state $X^{1}\Sigma^{+}$; the data comprised published frequencies and wavenumbers of pure rotational and vibration-rotational transitions. Since publication of that paper, errors in listed parameters and deficiencies in the discussion have been discovered; thus we present corrected tables here and explain those corrections. During the same period further experiments yielded measurements of pure rotational transitions of increased range and precision (2, 3), and extended theoretical analysis (4, 5) provided insight into adiabatic and nonadiabatic effects applicable to this species of LiH.

The theoretical background is presented in detail elsewhere (6). The parameters in the accompanying tables are introduced implicitly or explicitly within two relations for discrete molecular energies \hat{E}_{ul} (in units of wavenumber) within a particular electronic state, or the vibration–rotational terms. In the equation (6)

$$\tilde{E}_{vJ} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} (Y_{kl} + Z_{kl}^{v\text{Li}} + Z_{kl}^{v\text{Li}} + Z_{kl}^{v\text{Li}} + Z_{kl}^{v\text{H}}) \times \left(v + \frac{1}{2}\right)^{k} [J(J+1)]^{l},$$
[1]

the superscripts to Z denote the following: Li or H denotes the contribution of the specified atomic center, v denotes the vibration–rotational contributions of individual nuclei, and r denotes their additional rotational contributions; term coefficients Y_{kl} and various Z_{kl} contain within them the radial coefficients c_j , s_j , t_j , and u_j of Li and H as explained elsewhere (6); dependence of \tilde{E}_{vJ} , Y_{kl} , and all Z_{kl} on isotopic species is suppressed. In the equation

$$\tilde{E}_{vJ} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} U_{kl} \mu_i^{-(1/2)k-l} \left(v + \frac{1}{2} \right)^k$$

$$\times [J(J+1)]^l [1 + m_e (\Delta_{kl}^{\text{Li}}/M_a + \Delta_{kl}^{\text{H}}/M_b)],$$
[2]

coefficients U_{kl} and $\Delta_{kl}^{\text{Li,H}}$ are assumed to be independent of nuclear mass, as all dependence on mass is taken into account through the individual atomic masses M_{Li} and M_{H} and the molecular reduced mass μ_i (7). After Eq. [2] was applied empirically (7), other authors (8, 9) emphasized in its usage the necessity for U_{kl} to be constrained so that (for instance) U_{kl} with l > 1 are functions of $U_{k,0}$ and $U_{k,1}$. The conventional method for imposing such constraints involves, implicitly or explicitly, application of a function for potential energy. Then fitting wavenumbers of spectral transitions to Eq. [2] becomes almost a problem of linear regression in suitable variables to yield the independent parameters U_{kl} , l = 0 and 1, and $\Delta_{kl}^{\text{Li,H}}$, requiring no initial values of these parameters (1). In contrast, fitting the same spectral data through Eq. [1] to various radial coefficients involves nonlinear regression, an iterative process that requires initial estimates of parameters.

We applied these separate approaches to fit 594 measurements of pure rotational and vibration-rotational transitions of LiH as follows. The pure rotational transitions (10-12) in the previous data set (1) were augmented with more precise and extensive recent measurements (2, 3), and the vibration-rotational transitions (12) in the previous data were supplemented by a few further transitions (13) that are not duplicated. Some pure rotational transitions were hence duplicated from independent measurements in three sets (2, 3, 12); we adopted this procedure because these measurements did not provide in one single set the complete range over available variations of rotational and vibrational quantum numbers and of isotopic species. Rather than the inconsistent masses previously used (1) in error, atomic masses in the present analysis are those reported in 1993 (14), which for ⁶Li and ⁷Li differ significantly from earlier values.

According to the procedure previously described (1), these data were fitted to differences between energy terms according to Eq. [2] to yield the parameters in the first column of Table 1. By means of analytic relations for both c_j , in terms of Y_{kl} (6, 15), and their estimated standard errors δc_j , propagated (16) from errors of the principal U_{kl} , these values, also presented in Table 1, were generated within the same extended program. The same data were fitted with the program Radiatom (6) implicitly to Eq. [1] but directly to parameters in pertinent radial functions to yield the values in Table 2; during this fit t_0^{Li} and t_0^{H} were constrained to values consistent with their relations to the known electric dipolar moment and rotational g factor, as explained previously (1), but no other parameter was constrained to a finite value. In particular, we omitted parameters for nonadiabatic vibrational effects $s_0^{\text{Li,H}}$ previously constrained (1) implicitly to values appropriate for an assumed dipolar moment; subsequent work (4) demonstrated this assumption to be invalid. By means of analytic expressions for Y_{kl} and various Z_{kl} in terms of radial coefficients (6), the program Radiatom generated primarily values of c_j , t_j , and u_j , and secondarily values of U_{kl} and $\Delta_{kl}^{\text{Li,H}}$, presented in the last column of Table 1.

As a result of the direct fit to Eq. [2], 8 parameters U_{kl} , 3 Δ_{kl}^{Li} , and 9 Δ_{kl}^{H} —in total 20 fitted parameters—plus 16 further, constrained parameters U_{kl} sufficed to reproduce 594 measurements with a normalized standard deviation $\hat{\sigma} = 1.09$. Through Eq. [1] the fit required only 18 adjusted parameters— $U_{0,1}, U_{1,0}, c_i$ with $1 \le j \le 6, t_1^{\text{Li}}, u_1^{\text{Li}}, u_2^{\text{Li}}, t_1^{\text{H}}, t_2^{\text{H}}$, and u_i^{H} with $1 \le i \le 5$ —plus two constrained parameters t_0^{Li} and t_0^{H} , with $\hat{\sigma} =$ 1.12. Comparison between columns of Table 1 indicates satisfactory agreement of values from the two approaches within specified standard errors; minor differences are expected because fitting models are inequivalent, but the nature of the models precluded the use of exactly equivalent sets of parameters that could be significantly evaluated. The normalized standard deviations of the two fits differ immaterially. An advantage of Eq. [2] is its almost linear model, but its disadvantage is that its parameters (adjusted and constrained) are numerous and have no intrinsic physical meaning. An advantage of Eq. [1] is that its parameters have minimum number and maximum chemical and physical significance (defining radial functions within the concept of separate electronic and nuclear motions), whereas its disadvantage is the nonlinear nature of the model, which requires an iterative process and initial values of parameters.

Previous discussion (1) of truncation of Eq. [2] was based on an incorrectly interpreted theoretical basis of this equation (8). If corrections $Y_{kl}^{(2)}$ (or $U_{kl}^{(2)}$) are absorbed in parameters $\Delta_{kl}^{\text{Li,H}}$, as previously explained (8), there exists a direct correspondence between the potential-energy coefficients c_j (or equivalent coefficients in other functions) and the leading

 TABLE 1

 Values of Parameters U_{kl} (m⁻¹ $u^{[(1/2)k+l]}$), $\Delta_{kl}^{1i,H}$, and c_l^{a}

k 1	U _{kl} (eq. 2)	U _{kl} (eq. 1)
1 0	131994.702±0.12	131994.747±0.110
2 0	-2043.234±0.096	-2043.310
30	14.617±0.035	14.642
4 0	-0.2344±0.0043	-0.2386
0 1	662.71037±0.00010	662.71044±0.00011
11	-17.91258±0.00021	-17.91263
2 1	0.16078±0.00015	0.16065
3 1 /10-	³ -3.047±0.038	-2.924
0 2 /10	2 -6.682182	-6.682179
1 2 /10	3 1.1608	1.1606
2 2 /10	6 -8.5168	-8.1925
3 2 /10	7 -4.2407	-6.0777
0 3 /10	6 7.4300	7.4300
1 3 /10	8 -4 1089	-4.1146
2 2 /10	9 -5 4413	-5 2692
2 3 /10	9 -1 0722	-1 0733
0 4 /10	-1.0732	-1.0735
1 4 /10	-2.015/	-1.9916
2 4 /10	1.6764	1.3140
0 5 /10	1.8146	1.8147
1 5 /10	7.6932	7.6813
0 6 /10	-3.4489	-3.4474
1 6 /10	-2.3012	-2.3952
0 7 /10	21 7.0216	7.0176
0 8 /10-	24 -1.5030	-1.5054
1	Δ_{kl}^{Li} (eq. 2)	Δ_{kl}^{Li} (eq. 1)
1 0	-0.1570±0.0058	-0.1522
0 1	-0.1257±0.0013	-0.1256
02	-0.739±0.059	-0.846
k l	Δ_{kl}^{H} (eq. 2)	Δ_{k1}^{H} (eq. 1)
1 0	-0.72262±0.00083	-0.72359
2 0	-0.476±0.017	-0.506
0 1	-1.56293±0.00034	-1.56384
1 1	-0.7321±0.027	-0.8214
2 1	3.21±1.3	-1.49
02	-3.8983±0.0097	-3.8645
12	1.570±0.13	2.273
03	-8.93±0.21	-8.03
1 3	0	38.4
04	-12.90+1.8	-1.90
0 5	0	-4.55
	c _j (eq. 2)	c _j (eq. 1)
0 /m ⁻¹	6572479.5 <u>+</u> 8.3	6572483.3±9.9
1	-0.8972551±0.0000105	- 0.8972575±0.0000112
2	0.348156+0.000102	0.348088+0.000091
3	-0.08755+0.00035	-0.08766+0.00036
~ A	-0.04502+0.00340	-0 04269±0 00192
5		-0.0222±0.00183
s c	-0.0234 <u>+</u> 0.0066	-0.0222±0.0003
D	0.090±0.022	0.039/±0.0095

^{*a*} Uncertainties denote a single estimated standard error, derived either during the direct fit to the indicated parameters or, for c_j through Eq. [2], through additional code in the program to evaluate these uncertainties through error propagation according to analytic methods involving variance and covariance. The normalized standard deviation $\hat{\sigma}$ of the fit of 594 data is 1.09.

 TABLE 2

 Coefficients of Radial Functions and Other Molecular Properties of LiH $X^{1}\Sigma^{+}$, All Independent of Mass^a

j	cj	t ^{Li} j	t ^H j	u ^{Li} /10 ⁶ m ⁻¹	u ^H j/10 ⁶ m ⁻¹	
0	(6572483.3 ±9.9) m ⁻¹	[0.75335]	[-0.76823			
1	-0.8972575 ±0.0000112	0.105 <u>+</u> 0.056	1.4728 <u>+</u> 0.0094	-5.7362 ±0.0092	-5.1880 ±0.0017	
2	0.348088 ±0.000091		-0.994 ±0.088	12.077 ±0.082	3.2791 ±0.0112	
3	-0.08766 ±0.00036				-2.413 ±0.126	
4	-0.04269 ±0.00183				5.58 ±0.48	
5	-0.0222 ±0.0063				-12.63 ±2.7	
6	0.0397 ±0.0095					
$U_{1,0} = (131994.747\pm0.110) \text{ m}^{-1} \text{ u}^{\frac{1}{2}}$ $U_{0,1} = (662.710435\pm0.000105) \text{ m}^{-1} \text{ u}$ $k_{e} = (102.65115\pm0.00018) \text{ N m}^{-1}$ $R_{e} = (1.59491070\pm0.00000136) \times 10^{-10} \text{ m}$ range $1.25 \leqslant \text{ R}/10^{-10} \text{ m} \leqslant 2.20$						

^{*a*} Values enclosed in brackets are constrained; all parameters for which no value appears are constrained to zero. The normalized standard deviation ϑ of the fit of 594 data is 1.12, and the *F* value is 2.06×10^{15} .

term coefficients U_{kl} with l = 0 and 1. Accordingly all values of Δ_{kl}^{LH} in Table 1 absorb the effects of $Y_{kl}^{(2)}$ and no further parameters $U_{kl}^{(2)}(1)$ need be invoked. To estimate further values of c_j based on zero values of coefficients U_{kl} beyond those U_{kl} with finite values in a set evaluated from available spectra is impracticable because the particular U_{kl} to yield an additional coefficient c_j must be chosen arbitrarily and inconsistent values of other U_{kl} then result. For instance, with c_j in a particular set up to j = 6 in Table 1 or 2, when one tries to estimate c_7 by setting to zero one of $U_{4,1}$, $U_{3,3}$, $U_{2,5}$, $U_{1,7}$ or $U_{0,9}$, for LiH the range of consequent magnitudes of c_7 exceeds a factor 2, but for other molecules the range is much larger, and ranges of values of any further coefficient c_i expand rapidly.

Comparison (1) was made with results of Coxon (17) on similar spectral data. Further tests reveal that printed values (17) of all parameters R_e , c_j , $g_j^{\text{Li,H}}$ (as $t_j^{\text{Li,H}}$), and $h_j^{\text{Li,H}}$ (as $u_j^{\text{Li,H}}$) substituted in published expressions (6, 15) fail to reproduce the input data satisfactorily; the normalized standard deviation $\hat{\sigma}$ is 106. For this reason, apart from the inaccurate parameters previously reported (1), graphical comparison (1) of potential-energy functions with those of Coxon (17) would be meaningless. Such comparison of radial functions must logically take into account the error in each function propagated ultimately from errors of frequency measurements; by mistake the previous comparison (1) was not effected in this way.

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